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19 AESTRACT

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Pyyromethene-BF_2 Complexes as Laser Dyes

by

M. Shah, K. Thangaraj, M. L. Soong, L. T. Wohlford, J. H. Boyer, I. R. Politzer, and T. G. Pavlopoulos

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PYRROMETHENE–BF_2 COMPLEXES AS LASER DYES

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ABSTRACT

Condensations between 3–X–2,4–dimethylpyrroles (X = H, CH_3, C_2H_5, and $CO_2C_2H_5$) and acyl chlorides gave derivatives of 3,5,3′,5′–tetramethylpyrromethene (isolated as their hydrochloride salts): 6–methyl, 6–ethyl, 4,4′,6–trimethyl, 4,4′–diethyl–6–methyl, and 4,4′–dicarboethoxy–6–ethyl derivatives for conversion on treatment with boron trifluoride to 1,3,5,7–tetramethylpyrromethene–BF_2 complex (TMP–BF_2) and its 8–methyl (PMP–BF_2), 8–ethyl, 2,6,8–trimethyl (HMP–BF_2), 2,6–diethyl–8–methyl (PMDEP–BF_2), and 2,6–dicarboethoxy–8–ethyl derivatives. Chlorosulfonation converted 1,3,5,7,8–pentamethylpyrromethene–BF_2 complex to its 2,6–disulfonic acid isolated as the lithium, sodium (PMPDS–BF_2), potassium, rubidium, cesium, ammonium, and tetramethylammonium disulfonate salts and the methyl disulfonate ester. Sodium 1,3,5,7–tetramethyl–8–ethylpyrromethene–2,6–disulfonate–BF_2 complex was obtained from the 8–ethyl derivative of TMP–BF_2. Nitration and bromination converted PMP–BF_2 to its 2,6–dinitro– (PMDNP–BF_2) and 2,6–dibromo– derivatives. The time required for loss of fluorescence by irradiation from a sunlamp showed the following order for P–BF_2 compounds (10^{-3} to 10^{-4} M) in ethanol: PMPDS–BF_2, 7 weeks; PMP–BF_2, 5 days; PMDNP–BF_2, 72 h; HMP–BF_2, 70 h; and PMDEP–

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INTRODUCTION

In 1984, less than two decades after its discovery, a review described the dye laser as one of the most useful and practical of tunable coherent sources; it became serviceable over the spectral region 300 to 1300 nm by the frequency agility of over 600 laser dyes including cyanine, xanthene (e.g., rhodamine and fluoroscein), triarylmethane, acridine, azine, chlorophyll, polybenzenoid, coumarin, quinolone, oxazole, pyrazoline, and furan derivatives. Rhodamine dyes, e.g., R - 6G, gave laser activity over the spectral range 530 - 710 nm and were cited as the most important and most efficient group of all laser materials [1]. Laser dye activity was presumed to reflect a causal relationship with various ancillary properties including photostability, solubility and other interactions with solvent, fluorescence quantum yield, molar extinction of absorption, and minimal overlap of fluorescence with onset of absorption spectral regions, (S - S) and triplet-triplet (T - T) [1, 2]. Bathochromic and hyperchromic shifts were introduced by the substitution of auxochromic and antiauxochromic groups but this benefit was often offset by the ability of certain groups, e.g., nitro, cyano, and heavy atoms, to quench laser activity [1-3]. Since the known dyes were each deficient in one or more properties the search for new structures to offer superior performance standards was undertaken. Keywords: Laser Action in Pyrromethene-BF2

A recognition that the family of *syn*–bimanes A offered examples fulfilling many of the auxiliary conditions led to our discovery of their laser activity at 500 - 530 nm. Four bimanes A1 - 4 were as efficient (80 - 100%) as coumarin 30 (coumarin 515) (laser activity in

complex, Synthesis, Boron trifluoride, TMP, PMP, PMDEP, Unless ... PMPDS, ...

the same range) and showed improvements in photostability, solvent effects, and diminished overlap between fluorescence and absorption spectral regions (S - S and T - T) [3]. More recently the properties of certain pyrromethene–BF_2 complexes 10 and 11 also afforded candidates for laser dyes. We discovered laser activity at 533 nm from 1,3,5,7–tetramethylpyrromethene–BF_2 complex (TMP–BF_2) 10a in methanol in 1988 [4]. Superior activity was rapidly discovered in 1,3,5,7,8-pentamethylpyrromethene-BF_2 complex (PMP-BF_2) and its 2,6-dimethyl (HMP-BF_2), 2,6-diethyl (PMDEP-BF_2), and 2,6-disulfonic acid (isolated as the disodium salt PMPDS-BF_2) derivatives [5, 6]. Modest laser activity in the 2,6-dinitro derivative (PMDNP-BF_2) was exceptional [6] insofar as similar activity was not known for other dyes containing a nitro substituent. We wish to report the synthesis of pyrromethene-BF_2 complexes and further discovery and development of them as laser dyes.

BACKGROUND INFORMATION

A generally efficient condensation between an α–acylpyrrole and a pyrrole unsubstituted at an α–position was developed as a classical synthesis of the pyrromethene precursors to porphyrins [7]. More recently it accommodated investigations on the pyrromethene chromophore and fluorophore in tailored derivatives that included P–BF_2 compounds [4, 5, 8, 9]. When expressed in a simplified version $[R_2N(CR{=}CR)_n\ CR{=}NR_2]^+$ the cationic chromophore of a cyanine dye [1] included the pyrromethene cation (n = 4); however, the role of the latter has been limited to P–BF_2 compounds for laser activity [4-6], as fluorescent probes for medical and biological research [10], and in photodynamic therapy for cancer [11].

The unsubstituted pyrromethene B1 was unstable above -30 °C and gave a yellow solution (λ_{max} 400 nm) in *n*–pentane moistened with methanol at -60 °C [12]. Extensive alkylation brought about a bathochromic shift from 400 nm (log ϵ 4.35) for 3,5–dimethylpyrromethene B2 in pentane [12] to 447 nm (log ϵ 4.53) for 3,5,3′,5′–tetramethyl–4,4′–diethylpyrromethene B3 in ethanol [13]. Further bathochromic and hyperchromic shifts to 488 nm (log ϵ 5.00) and 528 nm (log ϵ 4.71) revealed related cationic pyrromethene chromophores for

the hydrobromide and BF_2–complex derivatives C and D of the pyrromethene B3 [10, 14, 15]. The band near 440 nm was shown to be polarized parallel, and shorter wave-length bands perpendicular, to the long axis of the chromophore [16].

Fluorescence quantum yields, $\bar{\Phi}$ 2.6 x 10^{-4} and 4.3 x 10^{-4} in ethanol, described comparable fluorophores for 3,5,3′,5′–tetramethyl–4,4′–diethylpyrromethene B3 and its hydrobromide C [17]. To account for these low quantum yields fluorescence quenching in a pyrromethene was variously correlated with proton tunneling [9], proton exchange between nitrogen atoms in the Z syn conformation, and photoisomerization at the exocyclic double bond [18, 19]; however, a deactivation of a pyrromethene S_1 state via exciplex formation, a process well known for polyamines [20], was not incompatible with the available information.

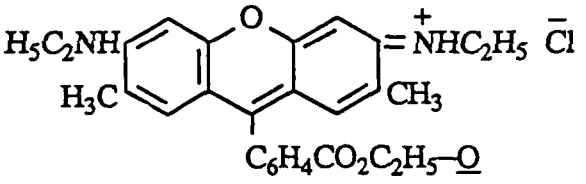
Chelation of boron difluoride by a pyrromethene bidentate anion was achieved by a treatment of a pyrromethene with boron trifluoride. Characterization of various pyrromethene–BF_2 (P–BF_2) derivatives included large extinction coefficients log $\epsilon \sim 5$ (comparable to the extinction coefficient shown for unchelated pyrromethene cations) and fluorescence quantum yields $\bar{\Phi}$ 0.33 to 0.81 [14, 17]. A similar value $\bar{\Phi}$ 0.31 was obtained for the corresponding $B(C_2H_5)_2$ complex E [17]. This thousand-fold enhancement in fluorescence that was brought about by boron chelation with the pyrromethene bidentate ligand was reminiscent of a similar fluorescence enhancement that was recently attributed to the chelation of zinc dichloride by the diamino moieties in the nonfluorescent 9,10–bis(((2–(dimethylamino)ethyl)methylamino)methyl)anthracene F; fluorescence quenching in the tetramine F was attributed to exciplex formation [21].

Strong fluorescence in a bidentate BF_2 complex with nitrogen and/or oxygen atoms as ligand termini was afforded by P–BF_2 derivatives 10 and 11 (Scheme) and by the recently patented dicarbonyl chelates G (laser activity range 455 - 635 nm) [22]. Although fluorescence was noted for BF_2 complexes H [23] and J [24] from 1–amino–7–imino–1,3,5–cycloheptatrienes and 8–amino– and 8–hydroxyquinoline these complexes were not examined for laser activity. BF_2 complexes with less unsaturation, e.g., the hexahydropyrromethene-BF_2 complex K with λ_{max} (C_2H_5OH) 320 nm (log ϵ 4.4) [25], were not examined for fluore-

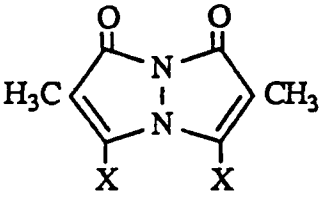
scence (< 400 nm) and laser activity. The hypsochromic shift ~ 120 nm relating P–BF_2 derivatives (λ_{max} ~ 440 nm) and the partially reduced structure K was typical of other cyanine dyes [1]. The structure assignment for PMP–BF_2 10b was supported by an X-ray crystallographic analysis [26].

Chelation of aluminum dichloride by a pyrromethene bidentate ligand gave an unstable orange solid; light absorption and emission data were not reported [25]. A different type of pyrromethene (P) – metal (M) chelate (P_2M) afforded by tetracordinate zinc, nickel, and copper showed weak fluorescence above 500 nm (Φ ~ 10^{-3}) [16, 18]. Pyrazoboles [dimeric 1–borylpyrazole chelates of dialkylboron (BR_2)] and the BF_2 complexes of 1,2,3,4–tetrahydro–1,10–phenanthroline were not fluorescent [27, 28].

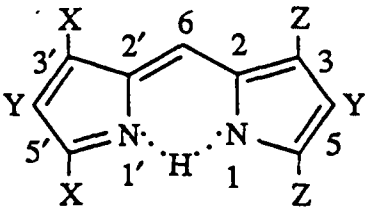
Laser activity was reported for a "boratriazinium" salt L and a "boradiazinium" salt M; however, preparations and structure characterizations for these molecules have not appeared in the literature [29].



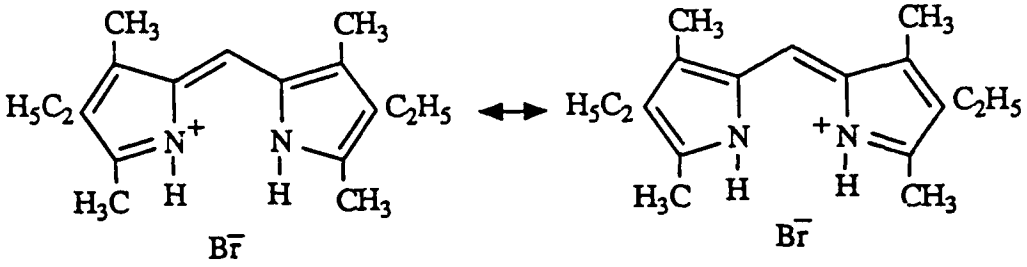
R - 6G•HCl



A1 X = $CH_2O_2CCH_3$
A2 X = $CH_2P(O)(OCH_3)_2$
A3 XX = $CH_2C(CO_2C_2H_5)_2CH_2$
A4 XX = $CH_2C(CO_2CH_3)_2CH_2$



B1 X = Y = Z = H
B2 X = Y = H, Z = CH_3
B3 X = Z = CH_3, Y = C_2H_5



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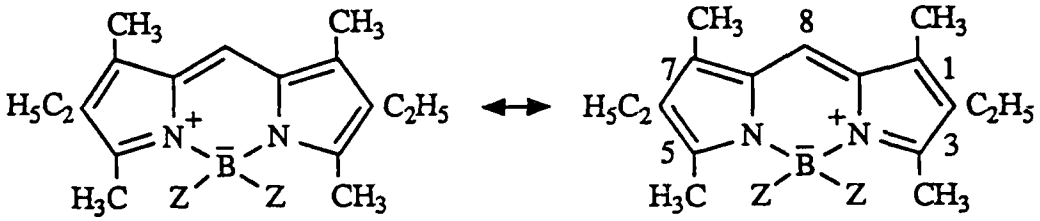
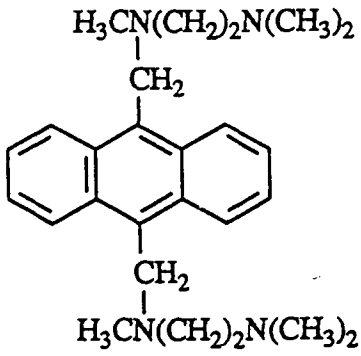


D Z = F
E Z = C_2H_5



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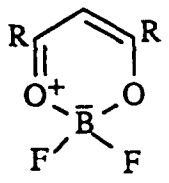
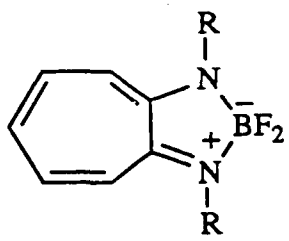


G R = $(CH{=}CH)_n$ Ar



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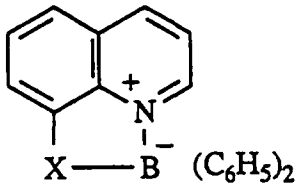
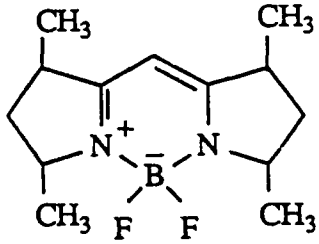


J X = NR, O



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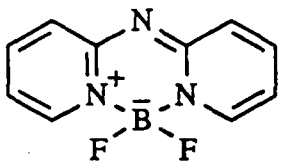

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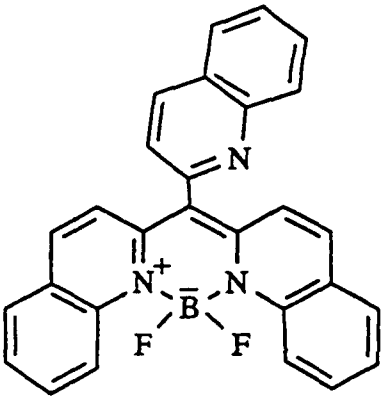
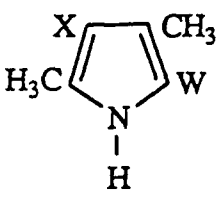


M

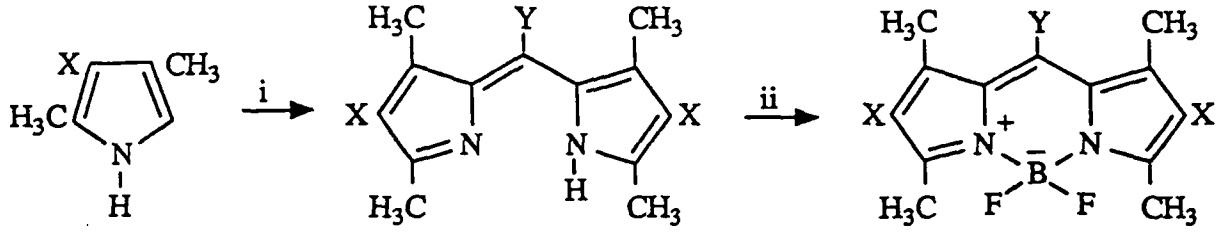
DISCUSSION AND RESULTS

A general pathway shown in the Scheme was followed for the conversion of pyrroles 1 - 4 to P–BF_2 10b - f. Kryptopyrrole 3 was commercially available; the pyrroles 1, 2, and 4 were obtained by adapting reported procedures for the hydrolysis and decarboxylation of diethyl 3,5–dimethylpyrrole–2,4–dicarboxylate 5 [30, 31] and ethyl 3,4,5–trimethylpyrrole-2–carboxylate 6 [32, 33] and the thermolysis of *tert*–butyl 3,5–dimethyl–4–carboethoxy-pyrrole–2–carboxylate 7 [34]. In reactions with appropriate acyl chlorides pyrroles 1 - 4 afforded the unstable intermediate pyrromethene derivatives 9b - f. These intermediates were isolated as hydrochloride salts and immediately converted, sometimes without purification, to their P–BF_2 derivatives 10b - f. As C-substitution increased the pyrromethene hydrochlorides became more stable and more amenable to isolation and characterization. According to a previously reported procedure 2–formyl–3,5–dimethylpyrrole 8 and 2,4–dimethylpyrrole 1 gave unisolated 3,5,3′,5′–tetramethylpyrromethene 9a [14].



5 W = X = $CO_2C_2H_5$
6 W = $CO_2C_2H_5$, X = CH_3
7 W = $CO_2C(CH_3)_3$, X = $CO_2C_2H_5$
8 W = CHO, X = H

In a typical chelation the hydrochloride salt of 3,5,3′,5′–tetramethylpyrromethene 9a gave TMP–BF_2 10a by treatment with boron trifluoride in the presence of triethylamine [14], or diisopropylethylamine (preferred) [16]. A similar conversion of the pyrrole derivati-



1 - 4 9a - f 10a - f

i = YCOCl; ii = $BF_3{\cdot}O(C_2H_5)_2$, R_3N

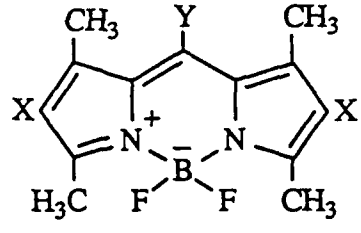
1, X = H; 2, X = CH_3; 3, X = C_2H_5; 4, X = $CO_2C_2H_5$

a X = Y = H; b X = H, Y = CH_3; c X = H, Y = C_2H_5;

d X = Y = CH_3; e X = C_2H_5, Y = CH_3; f X = $CO_2C_2H_5$, Y = C_2H_5

11k, m ← iv — 10b — iii → 11a - j

iii = $ClSO_3H$, base; iv = HNO_3 (k); Br_2 (m)



11a - m, Y = CH_3; 11n

a - e X = SO_3M, M = H (a), Li (b), Na (c), K (d), Rb (e), Cs (f);

g X = $S\bar{O}_3\overset{+}{N}H_4$; h X = $S\bar{O}_3\overset{+}{N}(CH_3)_4$; j X = SO_3CH_3; k X = NO_2;

m X = Br; n X = SO_3Na, Y = C_2H_5

Scheme

ve 4 afforded diethyl 1,3,5,7–tetramethyl–8–ethylpyrromethene–2,6–dicarboxylate–BF_2 complex 10f [25]. To extend the method to the preparation of PMP–BF_2 10b the precursor 3,5,3′,5′,6–pentamethylpyrromethene 9b was obtained directly from the treatment of 2,4-dimethylpyrrole 1 with acetyl chloride. A similar preparation afforded the 8–ethyl– deriva-

tive 10c from the precursor 3,5,3′,5′–tetramethyl–6–ethylpyrromethene 9c, in turn obtained from 2,4–dimethylpyrrole 1 and propionyl chloride. Complete C-substitution in a pyrromethene and its BF_2–complex was rarely encountered. In addition to the complex 10f other examples were found in chelations affording 1,2,3,5,6,7,8–heptamethyl– and 1,3,5,7,8–pentamethyl–2,6–diethylpyrromethene–BF_2 complexes (HMP–BF_2 and PMDEP–BF_2) 10d, e.

Electrophilic sulfonation in the 2– and 6– positions was reported for the complex 10a [15]. A similar substitution was initially useful in the preparation of the disodium (PMPDS-BF_2) and dimethyl 1,3,5,7,8–pentamethylpyrromethene–2,6–disulfonate–BF_2 complexes 11c, j. Straightforward modifications led to the formation of other dimetal (Li, K, Rb, and Cs) salts 11b, d - f and the diammonium and the bistetramethylammonium 1,3,5,7,8–pentamethylpyrromethene–2,6–disulfonate–BF_2 complexes 11g, h. Other examples of complete C-substitution were discovered in electrophilic nitration and bromination to give the 2,6–dinitro (PMDNP–BF_2) and 2,6–dibromo derivatives 11k, m. These substitution reactions supported quasiaromaticity for the pyrromethene–BF_2 complexes, cf., D, a property characteristic of various metal chelates [35, 36] and further supported by proton nmr signals δ 6.00 to 7.62 for unsubstituted ring positions in P–BF_2 derivatives [13].

Laser activity for P–BF_2 complexes (Table) gave RE from 0 to 100. Presumably a heavy atom effect brought about inactivity (RE 0) for 2,6–dibromo–1,3,5,7,8–pentamethylpyrromethane–BF_2 complex 11m. Each of the P–BF_2 complexes 10a - f and 11a - n showed high molecular extinction coefficients (log ϵ_s 4 to 5) and high fluorescence quantum yields (Φ 0.3 to 1.0) (Table). Minimal T - T absorption in or near the fluorescence spectral region was determined for TMP–BF_2 10a [4], PMP–BF_2 10b [5] and for PMPDS–BF_2 11c (Figure). A value ϵ_T (567) = 1.5 x 10^3 L/mole cm for PMDEP–BF_2 10e was exceptionally low in comparison with ϵ_T (570) = 7.9 x 10^3 L/mole cm and ϵ_T (580) = 6.6 x 10^3 L/mole cm for rhodamine dyes 560 and 575 [6]. To avoid self-quenching through aggregation a dye concentration of about 10^{-4} M was generally sought. A hypsochromic shift in fluorescence from 534 to 509 nm for PMPDS–BF_2 11c in water was brought about by dilution from 10^{-3} to 10^{-8} M and attributed to diminished aggregation as dilution increased [37]. Although me-

thanol (preferred), ethanol, or water were solvents of choice for laser activity from many P–BF_2, other satisfactory solvents in certain instances included acetonitrile, chloroform, dimethylsulfoxide, N,N–dimethylformamide, dichloromethane, dioxane, ethyl acetate, ethylene glycol, and hexafluoroisopropanol. Since the use of water minimized problems of storage and disposal or recovery of large amounts of organic solvents water soluble dyes were sought. Aqueous solutions also offered thermo-optic properties of water that often improved laser activity [2].

Just as a reaction between a P–BF_2 complex and methanolic potassium hydroxide was attributed to an initial nucleophilic attack at the 8–position that led to destruction of the chromophore [25], a similar reaction was assumed to account in part for the loss of fluorescence from PMP–BF_2 10b in ethanol solution after exposure to sunlamp irradiation for 5 days. In contrast the loss of fluorescence from the complex 10b in dichloromethane required a similar exposure to irradiation for 21 days. A greater photolability was demonstrated in the loss of fluorescence from other P–BF_2 derivatives (10^{-4} M in ethanol): PMDNP–BF_2 10k after 72 h, HMP–BF_2 10d after 70 h, and PMDEP--BF_2 10e after 65 h; and from PMPDS–BF_2 11c (10^{-4} M in water) after 55 h. In methanol PMPDS–BF_2 11c was markedly more stable; the loss of fluorescence in a similar experiment required 7 weeks. When photostability was determined by the number of flashlamp pulses required to lower laser power efficiency by 50 percent the complex 11c in methanol or ethanol was discovered to be much more photostable than other known laser dyes (including other P–BF_2 derivatives) for the spectral region 530 - 560 nm [38, 39]. In one laboratory when methanol solutions were examined the complex 11c was six times more photostable than the dye R - 6G (9000 pulses vs 1500 pulses) [40].

A comparison of laser energy output as a function of flashlamp pump energy showed PMPDS–BF_2 11c in ethanol offered three times the power efficiency from coumarin 545 and was comparable in efficiency to rhodamine - 6G [5]. Because of its exceptional photostability in methanol PMPDS–BF_2 11c was selected for further examination. From flashlamp excitation (pulsewidth 2 μsec, risetime 0.7 μsec) with pump energy at 300 J in conjunc-

tion with an LFDL–8 laser a 30% improvement in power efficiency for PMPDS–BF_2 11c over R - 6G (each 10^{-4} M in methanol) was realized [41, 42]. In the presence of caffeine (a filter for light < 300 nm) PMPDS–BF_2 (10^{-4} M in methanol) gave an improvement (28 to 66%) in laser efficiency that was dependent on flashlamp pulse width (2.0 to 7.0 μsec) [38, 39]. In contrast with an enhancement in laser activity from 10^{-3} M aqueous solutions of R - 6G and other xanthene dyes brought about by the presence of β–cyclodextrin (10^{-2} M), the fluorescence of PNPDS–BF_2 (10^{-3} to 10^{-8} M) in water was unaffected by similar treatment [37]. An interest in the effect on laser activity by the formation of a salt between R - 6G (the free base) and 1,3,5,7,8–pentamethyl pyrromethene–2,6–disulfonic acid 11a was thwarted by failure to obtain a tractable product from their interaction. There was no improvement in laser activity from an equimolar mixture of the two dyes, R - 6G (as the hydrochloride salt) and PMPDS–BF_2 11c, in methanol.

EXPERIMENTAL

Spectral data was obtained from the following instruments: Pye-Unicam SP 200 and Sargent-Welch 3-200 IR, Varian EM 360A, and IBM AF200 NMR [43], Hewlett-Packard 5985 (70 eV) (GC-MS), Cary 17 (UV), and Perkin-Elmer LS-5B Luminescence Spectrometers. A dye laser was constructed at the Naval Ocean Systems Center [44]. It operated in the non-flowing (static) mode and had no tuning capability. The dye cell (2.5 mm diam., 50 mm long) had an eliptical cavity configuration of small eccentricity. The flashlamp EG & G model FX 139C-2, produced a pulse which had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [44, 45]. Laser energy outputs were measured with an accuracy of ± 5% by a Scientech 365 power and energy meter [46]. Light absorption, luminescence, and laser activity properties are described in the Table.

For each product the IR and EI-MS data agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wave length. H NMR spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard.

length. H NMR spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference; the central peak of the solvent multiplet signal was assigned: δ 77.00 ($CDCl_3$), 39.50 $(CD_3)_2(SO)$. Poor solubility precluded NMR analyses in many instances. Fluorescence quantum yields of the dyes were determined for methanol solutions with excitation at 450 and 460 nm by reference to acridine orange, $\bar{\Phi}$ 0.46 [14], in ethanol. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, Indiana and Galbraith Laboratories, Inc., Knoxville, Tenn. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [47] using McClure's method [48].

Solvents, reagents, and starting materials that were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrille, acetyl chloride, alumina, ammonium carbonate, ammonium chloride, benzene, boron trifluoride etherate, bromine, carbon tetrachloride, celite, cesium carbonate, chloroform–d, chlorosulfonic acid, deuterium oxide, dichloromethane, N,N–disopropylethylamine, N,N-dimethylformamide (DMF), dimethyl sulfoxide–d_6 (DMSO–d_6), *p*–dioxane, ethanol, ethyl acetate, hexane, hexafluoroisopropanol, hydrazine hydrate, lithium carbonate, isopropanol, isopropyl ether, kryptopyrrole (2,4–dimethyl–3–ethylpyrrole 3), magnesium sulfate, methanol, nitric acid, 2–methyltetrahydrofuran, petroleum ether, phosphoric acid, potassium bromide, potassium carbonate, potassium fluoride, propionyl chloride, rubidium carbonate, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), tetramethylammonium carbonate, toluene, triethylamine, and trifluoroethanol. Rhodamine 6-G and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaccus, NJ. Nitrogen was obtained from Air Products and Chemicals, Inc., Allentown, PA.

The following compounds were prepared according to the directions cited: ethyl 2,4-dimethylpyrrole–3–carboxylate 4 [34]; diethyl 3,5–dimethylpyrrole–2,4–dicarboxylate 5 [30, 31]; ethyl 3,4,5–trimethylpyrrole–2–carboxylate 6 [32]; *tert*–butyl 3,5–dimethyl–4–carboethoxypyrrole–2–carboxylate 7 [34]; 2–formyl–3,5–dimethylpyrrole 8 [12]; 3,5,3′,5′-tetramethylpyrromethene 9a (modified for isolation as its hydrochloride salt) [14]; 1,3,5,7-tetramethylpyrromethene–BF_2 complex 10a (modified procedure) [14]; and 4,4′–dicarboethoxy–6–ethyl–3,5,3′,5′–tetramethylpyrromethene 9g (modified for isolation as the hydrochloride derivative, mp 227 - 232° C (dec), EI-MS (relative abundance): 373 (100, M^+ –Cl)) [34].

2,4–Dimethylpyrrole 1. In an adaptation of a procedure [30] diethyl 3,5–dimethylpyrrole-2,4–dicarboxylate 5 (160.0 g, 0.66 mol) as a melt at 140 °C was treated with phosphoric acid (85%, 320 mL). The mixture was heated at 180 °C for 30 min and poured into aqueous sodium hydroxide (3.5 M, 3.5 L). Codistillation gave 3 L that was extracted with isopropyl ether (3 x 500 mL). The organic phase was dried (potassium carbonate) and concentrated to give a dark brown oil that distilled, 70 - 80 °C (10 mm), to give 2,4–dimethylpyrrole 1 as a colorless oil, 40.00 g (64%); bp 162 - 165 °C (lit. [30] 160 - 165 °C); ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 3H), 2.16 (s, 3H), 5.72 (s, 1H) 6.31 (s, 1H), 7.20 - 7.87 (br s, 1H). Similarly ethyl 3,4,5–trimethyl–2–carboxylate 6 was converted to 2,3,4–trimethylpyrrole 2 as a colorless solid, (67%), mp 37 - 38 °C (lit. [32] mp 36 - 38 °C).

3,5,3′,5′,6–Pentamethylpyrromethene Hydrochloride 9b. Acetyl chloride (35 mL, 0.49 mol) was added dropwise with stirring over a period of 15 min to a solution of 2,4–dimethylpyrrole 1 (20.0 g, 0.21 mol) in dichloromethane (150 mL). The reaction mixture was heated at 40 °C for 1 h, cooled to room temperature, diluted with petroleum ether (1.5 L) and triturated for 12 h to bring about the separation of 3,5,3′,5′,6–pentamethylpyrromethene hydrochloride 9b. It was isolated by vacuum filtration as a red-brown powder, 24.0 g (91%), mp 180 - 185 °C (dec); EI-MS (relative abundance): 214 (51.8) (M^+ –HCl); H NMR

($CDCl_3$): δ 2.02 (s, 6H); 2.20 (s, 6H); 2.49 (s, 3H); 6.20 (s, 2H) [43]. Instability precluded elemental analysis.

Similarly the hydrochloride salts of derivatives of 3,5,3′,5′–tetramethylpyrromethene were obtained. The pyrrole 1 and propionyl chloride gave the 6–ethyl– derivative 9c, 81%, mp 192 - 195 °C (dec). Anal. calcd for $C_{15}H_{21}N_2Cl$: C, 68.04; H, 7.99; N, 10.58. Found: C, 67.47; H, 7.80; N, 10.17. The pyrrole 2 and acetyl chloride gave the 4,4′,6–trimethyl derivative 9d, 80%, mp 210 - 212 °C (dec); H NMR ($CDCl_3$): δ 1.90 (s, 6H), 2.00 (s, 6H), 2.45 (s, 6H), 2.75 (s, 3H) [33]. Anal. calcd for $C_{16}H_{23}N_2Cl$: C, 68.94; H, 8.25; N, 10.05; Cl, 12.74. Found: C, 69.41; H, 7.72; N, 10.21; Cl, 12.97. The pyrrole 3 and acetyl chloride gave the 4,4′–diethyl–6–methyl derivative 9e, 77%, mp 185 - 186 °C (dec); H NMR ($CDCl_3$): δ 1.01 (t, 6H), 2.07 (s, 6H), 2.35 (q, 4H), 2.46 (s, 6H), 2.76 (s, 3H) [43]. Anal. calcd for $C_{18}H_{27}N_2Cl$: C, 70.47; H, 8.80; N, 9.13; Cl, 11.58. Found: C, 70.67; H, 9.00; N, 9.15; Cl, 11.73.

1,3,5,7,8–Pentamethylpyrromethene–BF_2 complex (PMP–BF_2) 10b. Triethylamine (15 mL, 113 mmol) was added at room temperature to a suspension of 3,5,3′,5′,6–pentamethylpyrromethene hydrochloride 9b (6.0 g, 24 mmol) in toluene (600 mL) and the mixture was stirred for 15 min. Boron trifluoride etherate (20 mL, 163 mmol) was added dropwise with stirring as a green fluorescence developed. The reaction mixture was heated (80 °C) for 15 min, cooled to 40 °C, washed with warm water (3 x 100 mL), dried (magnesium sulfate) and concentrated to give a dark brown solid. Flash chromatographic [49] separation of a solid mixture (silica gel, 250 g, 230 - 400 mesh, 60 Å, a mixture (80:20) of toluene and hexane) followed by concentration of the intense green-yellow fluorescent fractions gave PMP-BF_2 10b. It recrystallized from ethyl acetate as an orange crystalline solid, 4.1 g (66%) (see Table for other properties). In reactions with boron trifluoride the hydrochlorides of pyrromethenes 9c - f gave the corresponding P–BF_2 derivatives 10c - f (Table). ^{1}H NMR [43]: HMP–BF_2 10d ($CDCl_3$): δ 1.91 (s, 6H), 2.29 (s, 6H), 2.46 (s, 6H), and 2.57

(s, 3H); PMDEP–BF_2 10e ($CDCl_3$): δ 1.01 (t, 6H), 2.30 (s, 6H), 2.37 (q, 4H), 2.47 (s, 6H), and 2.57 (s, 3H).

Disodium 1,3,5,7,8–pentamethylpyrromethene–2,6–disulfonate–BF_2–complex (PMPDS-BF_2) 11c. A solution of chlorosulfonic acid (3.26 g, 28 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of PMP–BF_2 10b (3.65 g, 14 mmol) in dichloromethane (50 mL) at -50 °C. As the reaction mixture warmed slowly to room temperature a yellow solid separated. The disulfonic acid 11a was isolated by vacuum filtration and treated with water (600 mL). The aqueous solution was neutralized with sodium bicarbonate (2.52 g, 30 mmol). The solution was concentrated to 75 mL, and treated with ethanol (400 mL) to bring about the separation of the salt 11c. It was isolated by vacuum filtration, recrystallized from aqueous ethanol (80%) and dried in air to give a yellow-orange powder, 5.0 g (75%) (Table). The dilithium, dipotassium, dirubidium, dicesium, diammonium, and the bistetramethylammonium salts 11b, d - h (Table) were prepared in straightforward reactions. A similar conversion of 1,3,5,7–tetramethyl–8–ethylpyrromethene–BF_2 complex 10c gave disodium 1,3,5,7–tetramethyl–8–ethylpyrromethene–2,6–disulfonate–BF_2 complex 11n (Table).

Dimethyl 1,3,5,7,8–pentamethylpyrromethene–2,6–disulfonate–BF_2–complex 11j. To a cooled suspension of 1,3,5,7,8–pentamethylpyrromethene–BF_2–complex 10b (2.0 g, 7.6 mmol) in dichloromethane (30 mL) at -50 °C a solution of chlorosulfonic acid (3.6 g, 30 mmol) in dichloromethane (20 mL) was added dropwise. As the clear yellow solution warmed to room temperature a brown oil separated. It was treated with methanol (10 mL), stirred for 0.5 h at room temperature, concentrated to a brown viscous oil, treated with methanol (40 mL), and stirred to bring about the separation of a yellow-brown solid that was isolated by vacuum filtration, treated with methanol (100 mL), and heated (60 °C) for 0.5 h to complete an esterification. The solid ester 11j, 1.4 g (40%), was isolated and purified from methanol to give an orange-yellow powder (Table).

1,3,5,7,8–Pentamethyl–2,6–dinitropyrromethene–BF_2 complex (PMDNP–BF_2) 11k. After PMP–BF_2 10b (3.0 g, 11.5 mmol) was added to nitric acid (50 ml, 70%) at 0 °C the orange-red mixture was stirred at 0 °C for 1.5 h and poured into ice-water (200 ml) to precipitate the 2,6–dinitro derivative 11k as an orange solid isolated by filtration and washed with water. It recrystallized from ethyl acetate as an orange power, 2.9 g (Table).

1,3,5,7,8–Pentamethyl–2,6–dibromopyrromethene–BF_2 complex 11m. Bromine (16.0 g, 100 mmol) in dichloromethane (50 ml) was added dropwise to PMP–BF_2 10b (2.0 g, 7.6 mmol) in dichloromethane (150 ml) over a period of 10 m at 25 °C with stirring. An orange precipitate was separated, triturated with dichloromethane (150 ml), and dried to give the dibromo derivative 11m as an orange crystalline solid, 1.6 g (Table); ^{1}H NMR [43] ($CDCl_3$): δ 2.41 (s, 6H), 2.55 (s, 6H), and 2.60 (s, 3H).

Pyrromethene–BF_2 complexes photostability. A solution of 1,3,5,7,8–pentamethylpyrromethene–BF_2 complex (PMP–BF_2) 10b (0.10 g, 0.3 mmol) in ethanol (250 ml) was irradiated by a sunlamp (GE 275W) at a distance of 30 cm. Fluorescence at 500 nm became undetectable after 5 days. In similar experiments other P–BF_2 derivatives (10^{-4} M in ethanol) also lost fluorescence: PMDNP–BF_2 11k after 72 h, HMP–BF_2 10d after 70 h, and PMDEP–BF_2 10e after 65 h. Disodium 1,3,5,7,8–pentamethylpyrromethene–2,6–disulfonate–BF_2 complex (PMPDSBF_2) 11c (2.0 mg) in water (50 ml) lost its fluorescence at 492 nm after 55 h of similar irradiation; when water was replaced with methanol the duration of fluorescence was 7 weeks. In brown bottles all P–BF_2 compounds were indefinitely stable to storage at 25 °C.

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REFERENCES

[1] M. Maeda, "Laser Dyes," Academic Press, Tokyo, Japan, 1984.

[2] C. M. Lau, I. R. Politzer, K. Thangaraj, G. Kumar, V. T. Ramakrishnan, E. D. Stevens, J. H. Boyer, and T. G. Pavlopoulos, Heteroatom Chem.,__ ,1990,___.

[3] H. Zollinger, "Color Chemistry," VCH, Weinheim, 1987.

[4] T. G. Pavlopoulos, M. Shah, and J. H. Boyer, Applied Optics, *27*, 1988, 4998.

[5] T. G. Pavlopoulos, M. Shah, and J. H. Boyer, Optics Commun., *70*, 1989, 425.

[6] T. G. Pavlopoulos, J. H. Boyer, M. Shah, K. Thangaraj, and M. -L. Soong, Optics Commun., submitted.

[7] A. H. Corwin, "The Chemistry of Pyrrole and its Derivatives," in R. C. Elderfield, "Heterocyclic Compounds," Vol 1, John Wiley and Sons, New York, 1950.

[8] S. E. Braslavsky, A. R. Holzwarth, and K. Schaffner, Angew. Chem. Int. Ed. Engl., *22*, 1983, 656.

[9] J. A. Pardoen, J. Lugtenburg, and G. W. Canters, J. Phys. Chem., *89*, 1985, 4272.

[10] E. Vos de Wael, J. A. Pardoen, J. A. Van Koeveringe, and J. Lugtenburg, Recl. Trav. Chim. Pays-Bas, *96*, 1977, 306.

[11] L. R. Morgan, A. Chaudhuri, L. E. Gillen, J. H. Boyer, and L. T. Wolford, "Pentamethylpyrromethene boron difluoride complex in human ovarian cancer photodynamic therapy," Optical Engineering/Laser '90 Conference, Los Angeles, CA, January 1990.

[12] J. A. Van Koeveringe and J. Lugtenburg, Recl. Trav. Chim. Pays-Bas, *96*, 1977, 55.

[13] R. W. Guy and R. A. Jones, Aust. J. Chem., *18*, 1965, 363.

[14] A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, J. Chem. Soc., 1959, 3416.

[15] H. J. Wories, J. H. Koek, G. Ladder, and J. Lugtenburg, Recl. Trav. Chim. Pays-Bas, *104*, 1985, 288.

[16] H. Falk, O. Hofer, and H. Lehner, Monatsh. Chem., *105*, 1974, 169.

[17] A. Holzwarth, H. Lehner, S. E. Braslavsky, and K. Schaffner, Liebig's Ann. Chem., 1978, 2002.

[18] H. Falk and F. Neufingerl, Monatsh. Chem., *110*, 1979, 987.

[19] H. Falk, K. Grubmayr, and F. Neufingerl, Monatsh. Chem., *108*, 1977, 1185.

[20] M. Gordon and W. R. Ware, Eds., "The Exciplex," Academic Press, New York, 1975.

[21] M. E. Huston, K. W. Haider, and A. W. Czarnik, J. Amer. Chem. Soc., *110*, 1988, 4460.

[22] H. Hartmann, R. Hultzsch, H. D. Ilge, B. Friedrich, J. Hebenstreit, D. Fassler, and U. Meinel, Ger. (East) DD 255,884; Chem. Abstr., *104*, 1986, 139107z; P. Czerney, C. Igney, G. Haucke, and H. Hartmann, Z. Chem., 1988, 23.

[23] H. E. Holmquist and R. E. Benson, J. Amer. Chem. Soc., *84*, 1962, 4720.

[24] E. Hohaus and F. Umland, Chem. Ber., *102*, 1969, 4025.

[25] A. Treibs and F. -H. Kreuzer, Liebig's Ann. Chem., *718*, 1968, 208; *721*, 1969, 116.

[26] C. L. Picou, E. D. Stevens, M. Shah, and J. H. Boyer, Acta Cryst. Soc. C, in press.

[27] S. Trofimenko, J. Amer. Chem. Soc., *89*, 1967, 3165, 3170; *92*, 1970, 5118.

[28] G. Klebe, K. Hensen, and H. Fuess, Chem. Ber., *116*, 1983, 3125.

[29] D. Basting, F. P. Schafer, and B. Steyer, Appl. Phys., *3*, 1974, 81.

[30] A. Treibs and L. Schulze, Liebig's Ann. Chem., *739*, 1970, 225.

[31] H. Fischer, Organic Syntheses, Coll. Vol II, 1943, 202, 217.

[32] J. E. Bullock, A. W. Johnson, E. Markham, and K. B. Shaw, J. Chem. Soc., 1958, 1430.

[33] P. S. Clezy and A. W. Nichol, Aust. J. Chem., *11*, 1965, 1835.

[34] A. Treibs and K. Hintermeier, Chem. Ber., *87*, 1954, 1167; J. Liebigs Ann. Chem., *592*, 1975, 11.

[35] J. P. Collman, Angew. Chem. Intern. Ed. Engl., *4*, 1965, 132.

[36] J. P. Collman, "The Chemistry of Quasiaromatic Metal Chelates," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 78.

[37] I. R. Politzer, K. T. Crago, S. Garner, J. Joseph, J. H. Boyer, and M. Shah, International Conference on Lasers '89, New Orleans, LA, December 1989, Technical Digest HN. 10.

[38] J. H. Boyer, M. Shah, T. G. Pavlopoulos, and S. E. Neister, Sixth European Symposium on Organic Compounds, Belgrade, Yugoslavia, September 1989, Book of Abstracts, p 2.

[39] Personal communication from Dr. S. E. Neister, Phase-R Corporation.

[40] Personal communication from Dr. J. J. Ehrlich and Wayne Davenport, U. S. Army Missile Command, Redstone Arsenal.

[41] J. H. Boyer, M. Shah, K. Thangaraj, L. T. Wolford, T. G. Pavlopoulos, and J. Hsia, International Conference on Lasers '89, New Orleans, LA, December 1989, Technical Digest HN. 11.

[42] Personal communication from Dr. James Hsia, Candela Corporation.

[43] We are indebted to Dr. Harry Ensley, Tulane University, for the use of the IBM instrument.

[44] T. G. Pavlopoulos, Spectrochim. Acta, *42A*, 1986, 47.

[45] T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, and C. M. Lau, J. Appl. Phys., *60*, 1986, 4028.

[46] T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, and C. M. Lau, Optics Comm., *64*, 1987, 367.

[47] T. G. Pavlopoulos and D. J. Golich, J. Appl. Phys., *64*, 1988, 52.

[48] D. J. McClure, J. Chem. Phys., *19*, 1951, 670.

[49] W. Clark Still, M. Kahn, and A. Mitra, J. Org. Chem., *43*, 1978, 2923.

Table

Pyrromethene–BF_2 Complexes

Part I

No.	Yield %	mp °C	Formula	Calculated, % Found, %
10b	66	254 - 257 dec	$C_{14}H_{17}N_2F_2B$	C, 64.15; H, 6.53; N, 10.74 C, 64.34; H, 6.71; N, 10.84
10c	45	214 - 216	$C_{15}H_{19}N_2F_2B$	C, 65.24; H, 6.92; N, 10.15 C, 64.97; H, 6.88; N, 10.05
10d	34	286 - 287 dec	$C_{16}H_{21}N_2F_2B$	C, 66.20; H, 7.24; N, 9.65 C, 66.23; H, 7.35; N, 9.57
10e	34	207 - 208	$C_{18}H_{25}N_2F_2B$	C, 67.92; H, 7.86; N, 8.80 C, 67.88; H, 8.06; N, 8.79
11b	84	> 280	$C_{14}H_{25}N_2O_6F_2BS_2Li \cdot 2H_2O$	C, 35.74; H, 3.19; N, 5.95 C, 36.16; H, 3.50; N, 5.97
11c	75	> 300	$C_{14}H_{15}N_2O_6F_2BS_2Na_2$	C, 36.07; H, 3.24; N, 6.01 C, 36.42; H, 3.35; N, 6.14
11d	82	> 280	$C_{14}H_{15}N_2O_6F_2BS_2K_2$	C, 33.79; H, 3.01; N, 5.62 C, 33.91; H, 3.02; N, 5.62
11e	62	> 280	$C_{14}H_{15}N_2O_6F_2BS_2Rb_2$	C, 28.42; H, 2.53; N, 4.73 C. 28.36; H, 2.45; N, 4.69
11f	57	> 280	$C_{14}H_{15}N_2O_6F_2BS_2Cs_2$	C, 24.49; H, 2.18; N, 4.08 C, 24.58; H, 2.18; N, 4.13
11g	60	> 300	$C_{14}H_{23}N_4O_6F_2BS_2$	C, 36.85; H, 5.08; N, 12.28 C, 36.91; H, 5.02; N, 12.20
11h	78	281 - 282 dec	$C_{22}H_{39}N_4O_6F_2BS_2 \cdot H_2O$	C, 45.05; H, 7.05; N, 9.55 C, 45.29; H, 6.73; N, 9.50
11j	40	218 - 222 dec	$C_{16}H_{21}N_2O_6F_2BS_2$	C, 42.67; H, 4.70; N, 6.22 C, 42.54; H, 4.76; N, 5.96
11k	71	279 - 281 dec	$C_{14}H_{15}N_4O_4F_2B$	C, 47.70; H, 4.26; N, 15.90 C, 48.18; H, 4.46; N, 15.94
11m	50	300 - 302 dec	$C_{14}H_{15}N_2Br_2F_2B$	C, 40.00; H, 3.57; N, 6.66 C, 40.13; H, 3.67; N, 6.59
11n	69	> 260	$C_{15}H_{17}N_2O_6F_2BS_2Na_2$	C, 37.52; H, 3.57; N, 5.84 C, 38.20; H, 3.79; N, 5.75

Table

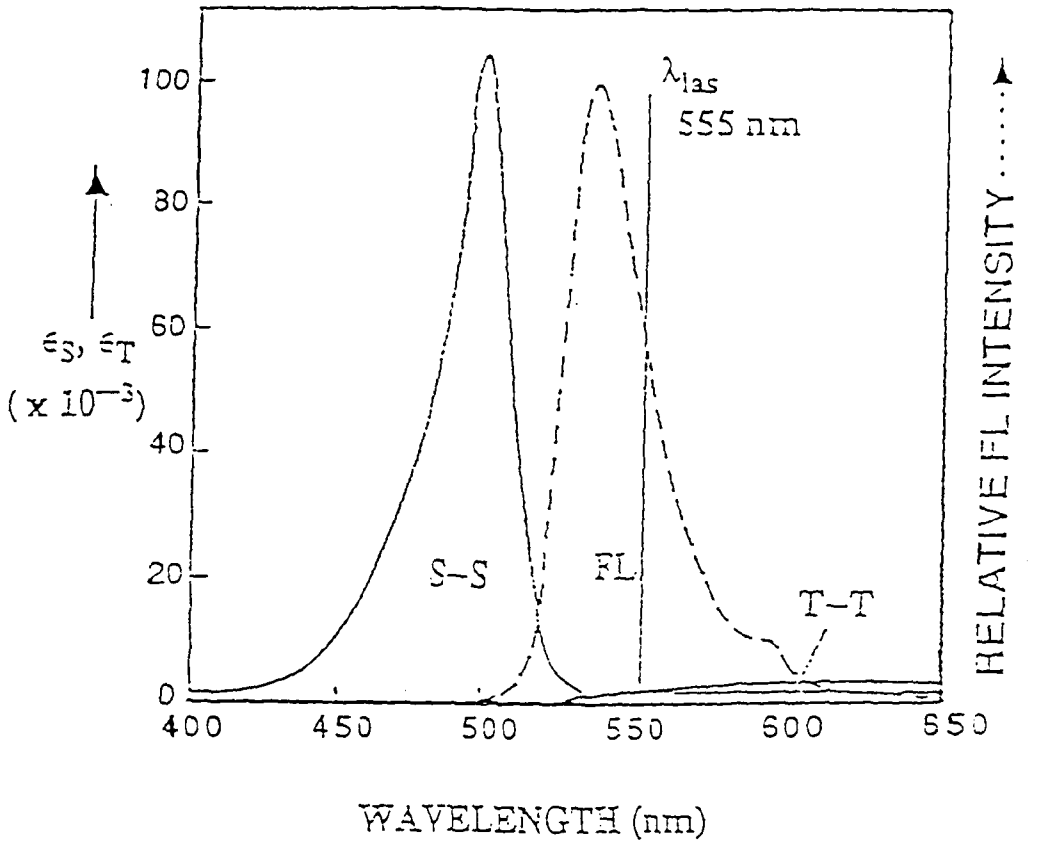
Pyrromethene-BF_2 Complexes

Part II[a]

No.	λ_{max} nm	log ϵ	λ_{Fl} nm	Φ	λ_{las} nm	RE[b] %	No.	λ_{max} nm	log ϵ	λ_{Fl} nm	Φ	λ_{las} nm	RE[b] %
10a	505	4.92	516	0.80	533	30	11d	498	4.96	534	0.78[e]	556	100
10b	493	4.90	519	0.99	542	100	11e	497	4.91	533	0.88[e]	553	95
10c	495	4.99	517	1.0	546	90	11f	497	4.91	531	0.81[e]	553	95
10d	518	4.67	543	0.70[c]	570	75	11g	496	4.92	533	0.90[e]	557	95
10e	517	4.81	546	0.83[c]	570	100	11h	497	4.97	535	0.89[e]	556	95
10f	493[d]	4.97[d]	531	0.38[c]	556	50	11j	483[f]	4.82	520[f]	0.82[g]	554[f]	35
11b	497	4.96	533	0.62[c]	554	65	11k	493	4.62	533	[h]	[h]	[h]
11c	492	4.86	533	0.73[e]	560	90	11m	516[f]	4.81	546[f]	0.45[g]		
							11n	498	4.90	530	0.44[c]	555	50

[a] Methanol was used as solvent except where noted otherwise. [b] Relative Efficiency in laser power output. RE 100 assigned to PMP-BF_2 10b. RE 30 observed for Coumarin 545 (ref 5). [c] In ethanol. [d] λ_{max} 495 nm (log ϵ 5.26) (ref 23). [e] In water. [f] In a mixture (9:1) of methanol and dichloromethane. [g] In dichloromethane. [h] Due to photoinstability the data was not reproducible

Figure. Absorption and luminescence for PMPDS–BF_2 complex 11c. T - T absorption: 1 x 10^{-4} M in α–methyltetrahydrofuran at 77 °K. S - S absorption and fluorescence: 1 x 10^{-4} M in ethanol. Broadband laser action: 2 x 10^{-4} M in ethanol.


100
80
60
40
20
0
400
450
500
550
600
650
ϵ_S, ϵ_T
(x 10^{-3})
λ_{las}
555 nm
S–S
FL
T–T
RELATIVE FL INTENSITY
WAVELENGTH (nm)

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